



An investigation of the Ni/carbonate interfaces on dual function materials in integrated CO₂ capture and utilisation cycles

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ABSTRACT

CO₂ capture and utilisation (CCU) is a promising strategy to effectively mitigate the adverse greenhouse effects caused by CO₂ emissions at an industrial scale. Through a process intensification strategy known as integrated CO₂ capture and utilisation (ICCU), CO₂ capture and catalytic CO₂ conversion can be achieved in a single process with the use of dual function materials (DFMs), which are both CO₂ sorbents and CO₂ conversion catalysts. Given the significantly different operating conditions of ICCU from conventional catalytic CO₂ hydrogenation, the catalytic mechanism of DFMs, especially during CO₂ hydrogenation, needs to be thoroughly investigated. In this study, the relationship between the nature of the Ni/carbonate interfaces and the performance of Ni-based DFMs over ICCU cycles is systematically investigated. A series of Ni/alkaline earth carbonate DFMs were synthesised with varying Ca:Mg ratios to simulate different metal-carbonate model interfaces. At 400 °C, CH₄ formation with nearly 100% CH₄ selectivity was achieved on Ni/CaCO₃ over 15 ICCU cycles. In general, Ni/CaCO₃ interfaces correspond to higher CO₂ conversion and higher CH₄ selectivity than Ni/MgCO₃ interfaces. Such trend may be attributed to the higher surface basicity of CaO and the higher thermal stability of CaCO₃. As a consequence, the hydrogenation of the Ni/CaCO₃ interface proceed via the formate pathway, in which carbonates are consecutively converted to surface formates, methoxyl, methyl species and eventually desorb as methane. This reaction model is applicable to the hydrogenation of both surface carbonate and bulk carbonates, although the former proceeds with much faster kinetics. On the weakly alkaline Ni/MgCO₃ interface, MgCO₃ preferentially decomposes to form gaseous CO₂, which is subsequently hydrogenated via the reverse-water-gas-shift pathway, with CO as the key reaction intermediate. Interestingly, in situ infrared spectroscopy shows similar surface significant species during the direct hydrogenation of DFMs and during the conventional catalytic hydrogenation of molecular CO₂, suggesting that the catalytic mechanisms during the two operating regimes are highly correlated.

1. Introduction

With the rapid urbanization and industrialization, the release of CO₂ has been dramatically increasing, e.g. from 20.5 Gt in 1990 to 36.9 Gt in 2022. [1,2] A large amount of CO₂ emissions and the resulting greenhouse effects, e.g., climate change, have posed an existential threat to the modern civilisation. Well-known consequences of climate change include rising sea level, [3] more frequent and destructive hurricanes,

[4] flooding, [5] etc. Hence, it is important and urgent to efficiently control and mitigate anthropogenic CO₂ emissions. The carbon capture and utilisation (CCU) scheme has been proposed to prevent the release of CO₂ and convert the captured CO₂ to fuels and chemicals that are conventionally derived from fossil fuels. Therefore, CCU has the potential to facilitate the transition to a defossilised economy. [6].

CCU involves firstly capturing CO₂ from emission sources, usually the combustion of fossil fuels (i.e., post-combustion capture). This can

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be achieved by scrubbing CO₂ from combustion flue gases using liquid amine solutions [7] or solid sorbents that are either highly porous [8–11] or suitably alkaline. [12] In particular, oxides of alkali metals or alkaline earth metals, e.g., CaO, [13,14] MgO, [15] Na₂O, [16] Na₂CO₃, [17,18] and Li-Al-oxides, [19] exhibit high CO₂ uptake capacities, fast uptake kinetics, low costs and high earth-abundance. [20] The captured CO₂ can be directly utilised for carbonating building materials, [21] filling fire extinguishers [22] and enhanced oil recovery (CO₂-EOR), [23] or catalytically converted to valuable products, [24,25] e.g., by hydrogenation using green hydrogen [26] to produce methane (methanation), CO (reverse water-gas-shift reaction), alcohols or long-chain hydrocarbons (Fischer-Tropsch synthesis). [27–30] The fuels and chemicals produced by CCU can also be considered as carriers storing the intermittently available renewable energy. [31] Therefore, CCU presents an opportunity to transition from a fossil-based chemical industry to an renewable one. [32].

In recent years, an integrated CO₂ capture and utilisation (ICCU) scheme, which achieves CO₂ capture and CO₂ conversion in a single reactor system, emerges as a unique process intensification approach for CCU. [33–36] During ICCU, the endothermic sorbent regeneration and the exothermic CO₂ hydrogenation reactions were achieved in a single step, thereby simplifying the process while saving energy. Doing so requires the availability of a dual function material (DFM) that is both a sorbent and a catalyst. [37] Intuitively, most designs of DFMs involve interfacing a catalytically active metal (for CO₂ reduction) with a solid CO₂ sorbent (for CO₂ capture). [33,36] Among many catalytic metal sites studied, e.g., Ru, Rh, Ni and Co, [38,39] Ni-based catalysts show satisfactory activity for CO₂ hydrogenation and relatively low costs. [40] Alkali metal oxides and alkaline earth metal oxides, such as Na₂O, [16, 41–43] LiAlO₂, [19] MgO [15,44] and CaO [45,46] are commonly employed to provide CO₂ capture functionalities. To further improve the catalytic conversion of the capture CO₂ and the long-term stabilities, the DFMs are promoted by the addition of reducible (e.g., CeO₂, [47–49] TiO₂, [50] ZrO₂, [51–53] etc.) and/or irreducible (e.g., SiO₂, [54,55] Al₂O₃, [56–58] MgO, [44] etc.), respectively. For example, Farrauto et al. [42] supported Ru/Na₂O DFMs on Al₂O₃, achieving stable performance over 50 cycles of ICCU owing to improved sintering resistance.

In recent years, there have been substantial advances in the development of ICCU cycles, including the development of high performance DFMs and more in-depth mechanistic studies of DFMs when employed in various applications of ICCU cycles. [17,37,59–62] On the other hand,

the catalytic mechanism for the direct hydrogenation of immobilised CO₂ (i.e., chemical bond to DFMs), remains inadequately understood. It is conducive that the direct interaction between the active metal sites and carbonated CO₂ sorbents in DFMs plays a critical role during the catalytic hydrogenation, and warrants more investigation. Broadly speaking, two reaction pathways could take place during the hydrogenation of carbonated DFMs: (i) the carbonates thermally decompose, releasing gaseous CO₂, which is subsequently adsorbed and converted on the active sites through conventional CO₂ hydrogenation mechanisms [63] and (ii) the hydrogen activated on the metal surface migrates to the carbonates, directly converting them to hydrogenated products, which eventually desorbs, [64] as schematically illustrated in Fig. 1. Regardless of the reaction pathway, key mechanistic insights, including (i) the interaction across the metal-carbonate interface, (ii) the roles of surface carbonates versus bulk carbonates, (iii) the reaction mechanism at the metal-carbonate interface, and (iv) the evolution of the metal-/carbonate interfaces over repeated ICCU cycles remain unclear.

To address the knowledge gaps stated above, this study employs model DFM structures consisting of Ni nanoparticles supported on a nanostructured, highly mesoporous MgCO₃, CaCO₃, or a mixture of both, [65–67] to investigate the hydrogenation of the captured CO₂, either in carbonate form or in gaseous form, during ICCU over the temperature range of 300–400 °C, where both CO₂ methanation and RWGS are thermodynamically favourable. Here, MgCO₃ and CaCO₃ represents two types of surface basicity and decomposition temperatures, [68–70] where are their mixtures are anticipated to possess properties that are in-between the two pure carbonates. The high mesoporosity of the carbonate support would facilitate the uniform dispersion of the Ni nanoparticles in the DFMs. By characterising the Ni/carbonate interfaces using gas adsorption/desorption experiments, electron microscopy and in situ infrared spectroscopy, the relationship between DFM structures, surface properties, catalytic pathways, reaction mechanisms, CO₂ conversion and selectivity are examined and elucidated. Lastly, through a comparative study, the analogy between the structural-functional relationship for DFMs over ICCU cycles and conventional CO₂ hydrogenation reactions is investigated.

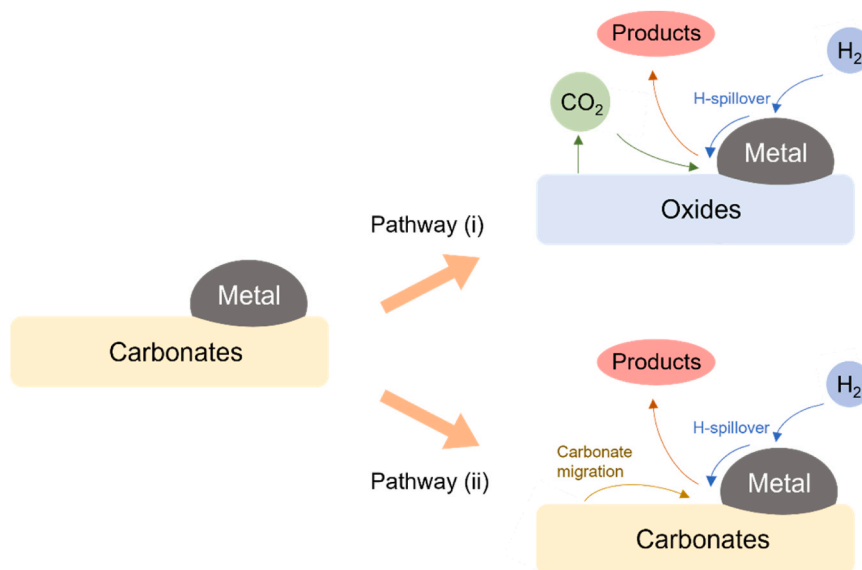


Fig. 1. Two possible reaction pathways of catalytic hydrogenation of immobilised CO₂ on DFMs during ICCU cycles.

2. Experimental

2.1. Materials

Calcium carbonate (CaO, 96–100.5%, FCC grade), magnesium oxide (MgO, 98.0–100.5%), nickel(II) acetate tetrahydrate (98%), citric acid (>99.5%) and ethanolamine ($\geq 98\%$) were purchased from Sigma-Aldrich, USA. Methanol (99.9% high-performance liquid chromatography grade) and ethanol absolute (99.96%) were purchased from VWR International, Sweden. All chemicals were directly used without further purification.

2.2. Catalyst preparation

Amorphous calcium carbonate (ACC) and mesoporous magnesium carbonate (MMC) suspensions were synthesized by a sol-gel method via carbonating the corresponding oxides in high-pressure CO_2 atmosphere. [65,67] The obtained ACC and MCC would have high specific surface areas (394–698 m^2/g) compared to commercial CaCO_3 and MgCO_3 (6.3–18.1 m^2/g). The NiO/carbonate samples were synthesized by a co-precipitation method, [71] as illustrated in Fig. 2. To make mixtures of MgCO_3 and CaCO_3 , the required amounts of ACC and/or MMC suspensions were mixed. Separately, nickel acetate was dissolved in methanol to obtain a clear solution. Then, the nickel acetate solution was added to the mixed suspension. The formed mixture was stirred for 30 min, which allowed the deposition of the NiO precursors onto the carbonate substrates. Afterwards, ethanolamine was added as the stabiliser, while the mixture was left for a further 5 min. To evaporate methanol, the mixture was heated at 150°C for 1 h, and then dried at 250°C in air for 20 h to receive fresh DFMs, which primarily consisted of NiO supported on mesoporous carbonates. The loading of NiO in each fresh DFMs was also verified by inductively coupled plasma atomic emission spectrometry (ICP-AES). Prior to reaction, the fresh DFMs were reduced in 10 vol% H_2/N_2 gas at 400°C for 2 h to produce Ni/carbonate DFMs. Using this method, Ni/carbonate DFMs with 5 different ACC:MCC mass ratios (viz. 1:0, 3:1, 1:1, 1:3 and 0:1) were prepared, each with a NiO loading of $\sim 10\text{ wt}\%$, and are denoted as Ni/Ca, Ni/Ca3Mg1, Ni/Ca1Mg1, Ni/Ca1Mg3 and Ni/Mg, respectively.

2.3. Catalyst characterisation

X-ray diffraction (XRD) was performed on a Bruker D8 Advance diffractometer with a $\text{K}\beta$ -filtered $\text{Cu K}\alpha$ source (40 kV, 40 mA, $\lambda = 0.154\text{ nm}$) to determine the change of the phase compositions of the fresh DFMs and when they are hydrogenated or spent after ICCU cycles.

The scans were collected continuously between $2\theta = 5^\circ - 120^\circ$, with a step size of 0.02° and a scan time of 0.5 s per step. The sample rotation was set at 15 rpm to minimise the effect of preferred orientation.

X-ray photoelectron spectroscopy (XPS) was conducted using a PHI Quantera II Scanning XPS Microprobe with $\text{Al K}\alpha$ radiation ($h\nu = 1486.6\text{ eV}$) to examine the change in the surface compositions of the DFMs over ICCU cycles. Prior to XPS measurements of the fresh, hydrogenated or spent DFMs, the samples were pretreated by sputtering with Ar plasma for 30 s to clean the surface and remove the oxidic passivation layers. The binding energies of the XPS spectra were calibrated using a reference C-C 1 s peak (B.E. = 284.6 eV).

The morphology of the DFMs (specifically, Ni/Ca, Ni/Ca1Mg1 and Ni/Mg) before and after H_2 reduction were examined using transmission electron microscopy (TEM), performed on a JEOL JEM2010 200 kV transmission electron microscope equipped with Gatan Erlangshen CCD camera for high-resolution image and video recording. Prior to TEM, 5 mg of the sample powders were dispersed in 5 mL absolute ethanol. The mixture underwent a 30-min ultrasonication to achieve a uniform dispersion. 1 drop of the suspension, collected from the top of the suspension, was dripped on a copper grid-supported holey carbon film, which was subsequently dried at 60°C for 30 min. The average Ni particle sizes were estimated based on the sizes of 10–20 Ni particles, sampled from the TEM images using ImageJ software.

The specific surface areas of the fresh, hydrogenated or spent samples were determined by the BET (Brunauer, Emmett and Teller) correlation, based on the N_2 adsorption-desorption isotherms of the samples measured at -196°C using a Micromeritics 3Flex. The samples were degassed at 150°C for 24 h on a Micromeritics VacPrep 061 degasser prior to the isotherm measurements.

H_2 -temperature programmed reduction (TPR) was conducted on a Micromeritics AutoChem II 2920 to analyse the reduction behaviour of NiO deposited on carbonate. The H_2 -TPR profiles reflect the extent of interaction between the reduced Ni and the alkaline earth metal oxide (e.g., MgO, CaO or a mixture of both). All gas flowrates, from this point onwards, are reported in standard temperature and pressure conditions (S.T.P), unless otherwise stated. In each measurement, 100 mg of fresh DFM sample was pre-calcined at 900°C for 1 h under an Ar flow of 50 mL/min to fully decompose all carbonates. Afterwards, the sample was cooled down to 40°C . Then, the inlet gas was switched to 50 mL/min of 10 vol% H_2/Ar . Subsequently, the temperature of the sample chamber was set to increase from 40°C to 900°C at a constant heating rate of $10^\circ\text{C}/\text{min}$. The off-gas was analysed on-line by a thermal conductivity detector (TCD) to determine the consumption of H_2 .

CO_2 -temperature programmed desorption (CO_2 -TPD) and is conducted using the same equipment as H_2 -TPR to analyse the basicity of

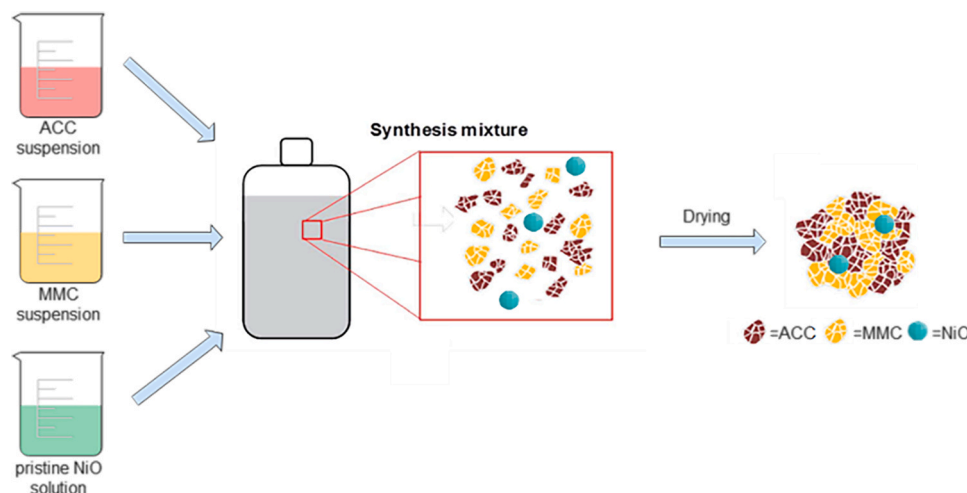


Fig. 2. Schematic illustration of the synthesis of fresh DFMs consisting of NiO/carbonates. The figure is adapted from [66].

the catalysts. In a typical CO₂-TPD measurement, 100 mg of fresh DFM sample was pretreated in 10 vol% H₂/Ar (50 mL/min) at 900 °C to fully decompose all carbonates, while reducing NiO to Ni. The reduced sample was cooled to 30 °C and purged with 50 mL/min of He. The sample was then treated in pure CO₂ (50 mL/min) for 30 min at 40 °C, facilitating saturated CO₂ adsorption. CO₂ desorption was achieved by heating the CO₂-saturated sample from 40° to 900°C with a heating rate of 10 °C/min, under a flow of pure He (50 mL/min). The amount of CO₂ desorbed was quantified by a TCD analyser. The gas outlet of the CO₂-TPD measurement was analysed by a mass spectrometer (MS).

CO pulse chemisorption was performed using the same equipment as TPR to measure the surface Ni metal dispersion. The fresh DFM sample (100 mg) was pretreated in 10 vol% H₂/Ar (50 mL/min) at 400 °C for 1 h and cooled to 40 °C. The reduced sample was then purged with He for 30 min until the TCD signal stabilised. Next, pulses of 10 vol% CO/He (10 mL per each pulse) were injected at 6 min intervals. The pulsed injection was stopped once the samples were saturated and no longer take up any more CO. The total amount of CO adsorbed by the catalysts were subsequently quantified to determine the surface Ni dispersion.

Thermogravimetric analysis (TGA) was carried out on a Mettler-Toledo TGA/DSC. The fresh DFM sample was first dewatered at 150 °C for 30 mins in 50 mL/min N₂. After the water removal, it was reduced in 50 mL/min of 5 vol% H₂/N₂ at a heating rate of 5 °C/min from 150° to 900°C. The reduced sample was then cooled to room temperature and subjected to temperature-programmed oxidation (TPO) from room temperature to 900 °C with a heating rate of 5 °C/min in 50 mL/min of air. The TPO results were used to determine the mass fraction of NiO in the sample prior to reduction.

In situ diffuse reflectance infrared Fourier transform spectroscopy (in situ DRIFTS) was performed using a Bruker Tensor II Fourier-transform spectrometer equipped with a liquid N₂-cooled MCT (Mercury Cadmium Telluride) detector, fitted with a PIKE Technologies DiffusIR optical accessory and a high temperature (–150 to 1000 °C) PIKE DRIFT environmental cell with ZnSe windows. In a typical measurement, 40 mg of fresh DFM sample consisting of a mixture of KBr and DFMs with a 2:1 mass ratio underwent the following pretreatment steps (1) reduction by 20 mL/min 25 vol% H₂/Ar for 1 h, (2) purge by 20 mL/min Ar for 15 min, (3) carbonation by 20 mL/min of 25 vol% CO₂/Ar; all carried out isothermally at 400 °C. Then, two types of DRIFTS experiments were carried out, (i) direct hydrogenation of the Ni/carbonate sample in 25 vol% H₂/Ar for up to 24 h and (ii) conventional CO₂ methanation in a 5/20/15 mixture of CO₂/H₂/Ar (i.e. co-feeding CO₂ and H₂) with a total flowrate of 40 mL/min for 60 min. Both experiments were conducted isothermally at 400 °C. Throughout the in situ DRIFTS experiments, IR spectra were continuously collected over the spectral range of 4000 – 600 cm^{–1} wavenumbers with a resolution of 4 cm^{–1} and 256 scans per spectrum.

2.4. Direct hydrogenation of Ni/carbonates

The direct hydrogenation experiments were performed in a fixed-bed reactor made of a quartz tube with a length of 50 cm, an inner diameter of 8 mm and a wall thickness of 1 mm. The setup of the reactor system is shown in Fig. S1 in Supporting Information (S.I.). To ensure that the active bed (i.e., where the DFM was located) operated under near-isothermal conditions, the packing arrangement, from bottom to top, was as follows: 1 cm-long rubber stopper, 30 mg silica wool, 25 g inactive Al₂O₃, 30 mg silica wool, DFM powders, and 30 mg silica wool. In each experiment, 100 mg of the fresh DFM samples (after pre-reduction in H₂/N₂ as described in Section 2.2, with size fraction of 0.6–2.0 mm) was loaded into the reactor and heated to 400 °C with a heating rate of 5 °C/min in 100 mL/min of 10 vol% H₂/N₂, and then kept isothermal at 400 °C for 1 h to ensure complete reduction of NiO to Ni. The reaction off-gas is analysed by on-line gas analysers (ABB, EL3020) equipped with different detector modules: Uras26 non-dispersive infrared spectrometer (for CH₄, CO and CO₂) and Caldos27

thermal conductivity analyser (for H₂).

2.5. ICCU cycles

The ICCU cycling experiments were conducted by cyclically feeding the packed DFMs with alternating gases of CO₂ and H₂, analogous to a chemical looping scheme. In each experiment, 100 mg sample (0.6–2.0 mm) was loaded in the quartz fixed bed reactor and calcined at 400 °C in pure N₂ (100 mL/min) for 1 h. Then, the sample was subjected to 15 ICCU cycles, each consisting of the following stages: (1) hydrogenation in 10 vol% H₂/N₂ (100 mL/min) for 1 h, (2) purge with N₂ (100 mL/min) for 30 min, (3) carbonation in 10 vol% CO₂/N₂ (100 mL/min) for 1 h, and (4) N₂ purge for 30 min. The temperature was kept isothermal at 400 °C during the ICCU cycles. Because of the focus of the present study is to investigate the Ni/carbonate interface rather than demonstrating high performance DFMs, we chose high space velocities and low DFM loading to facilitate the conversion of carbonates during the hydrogenation stage. As a result, the single-pass conversion of H₂ during the hydrogenation stage and uptake of CO₂ during the carbonation stage are expected to be low. The reaction off-gases are analysed by the same on-line gas analysers as described in Section 2.4.

2.6. Conventional catalytic CO₂ hydrogenation

The performance of the Ni/carbonate DFM for conventional catalytic CO₂ hydrogenation was evaluated using the same apparatus as described in Section 2.4. In each experiment, 100 mg of fresh DFM sample (with a sieve fraction of 0.6–2.0 mm) was loaded into the fixed bed reactor and reduced by 100 mL/min of 10 vol% H₂/N₂ at 400 °C for 2 h to convert the NiO to Ni metal to form the working catalysts. After reduction, the catalyst was exposed to a 60/15/25 vol% mixture of H₂/CO₂/N₂ with a total flow rate of 100 mL/min at different temperatures. The H₂:CO₂ ratio was fixed at 4:1, which corresponds to the desired stoichiometry for CO₂ methanation (see Equation 1). CO₂ hydrogenation was studied at 5 isothermal stages at 200, 250, 300, 350 and 400 °C, each lasting for 1.5 h. The outlet gas is channelled through a drying tube filled with particles of silica gel desiccant for moisture removal. Then, the dried effluent gas was sent to gas analysers (ABB EL3020) for compositional analysis.

3. Results

3.1. Catalyst characterisation

The synthesised fresh DFMs are comprehensively characterised to confirm the successful synthesis of the targeted formulae. First, the NiO loadings of the fresh DFMs were determined by thermogravimetric analysis (TGA), as shown in Fig. 3a. For all the fresh DFMs, 3 major weight losses are observed. The first drop at ~150 °C is attributed to the initiation of the reduction of NiO to Ni, accompanied by the decomposition of the organic residuals. The reduction of “bulk” NiO to Ni completes at ~200 °C, as shown and discussed in the TPR results below (Fig. 6). The second drop at ~350 °C is primarily associated with the decomposition of MgCO₃ to MgO. Therefore, the Ni active sites in DFM would have readily formed prior to the decomposition of MgCO₃ during the temperature-programmed hydrogenation experiments discussed in Section 3.2. The third drop at ~700 °C corresponds to the decomposition of CaCO₃ to CaO. The quantitative analysis of the second and third weight losses correspond well to the intended Ca:Mg ratios of the samples, as shown in Fig. 3b. The subsequent temperature-programmed oxidation (TPO) of the reduced DFMs (as shown in Fig. 3b) was then performed to measure the mass gain during the oxidation of Ni to NiO, which is used to estimate the mass fraction of NiO in the fresh DFMs. The TGA results tabulated in Table 1 show that, for all samples, the NiO mass fractions are close to 10 wt%, closely consistent with the targets of synthesis and the ICP results of these DFMs (Table S1).

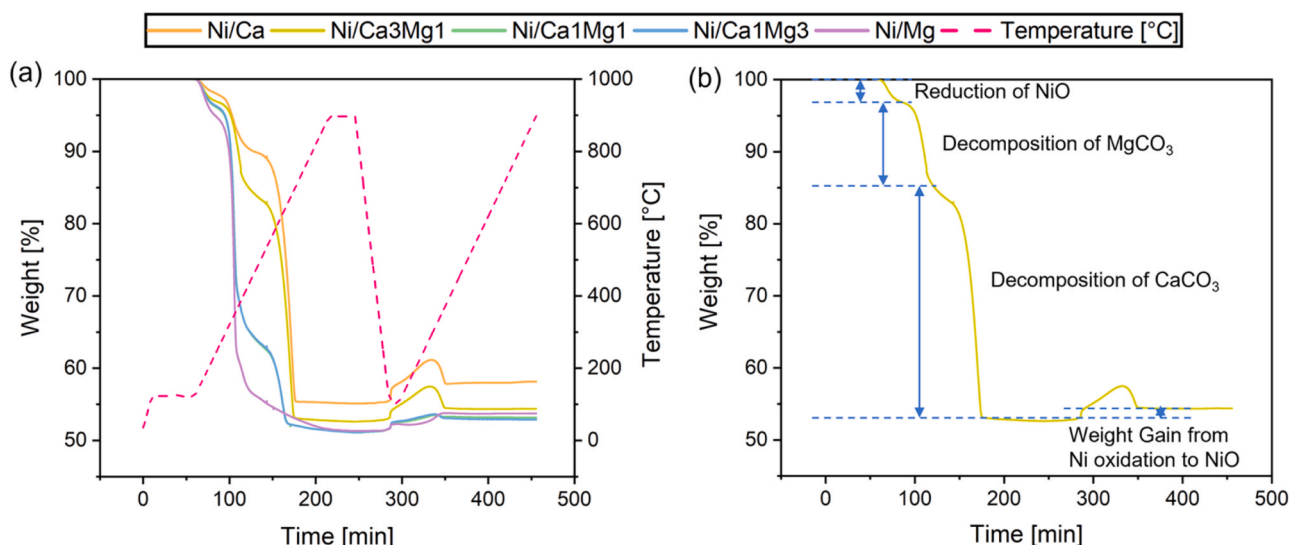


Fig. 3. (a) Weight loss - weight gain curves for all the fresh DFMs undergoing TGA analysis including temperature programmed reduction followed by temperature programmed oxidation, (b) Interpretation of weight loss - weight gain curve for the Ni/Ca3Mg1 sample in TGA.

Table 1
Summary of properties of Ni/carbonate DFMs.

Sample	S_{BET} [m^2/g]	Ni particle size [nm]		Ni dispersion [%]	Metallic Ni surface area [m^2/g]	NiO mass fraction [wt%]
		fresh	hydrogenated			
Ni/Ca	82	12 ± 6	13 ± 5	3.9	0.26	14.1
Ni/Ca3Mg1	115	-	-	5.9	0.39	8.3
Ni/Ca1Mg1	130	11 ± 4	13 ± 5	4.0	0.27	9.6
Ni/Ca1Mg3	127	-	-	2.3	0.14	8.3
Ni/Mg	178	19 ± 8	16 ± 9	0.8	0.05	11.3

Next, the porosity of the synthesised fresh DFMs were characterised by BET analysis. Table 1 shows the BET surface areas of the fresh DFMs. It can be seen that the BET surface area decreased with increasing CaCO_3 content. This trend is consistent with the pure carbonate sorbents without Ni loading, because mesoporous MgCO_3 is expected to exhibit a higher area than amorphous CaCO_3 [66]. Comparing the Ni-loaded samples with the Ni-free carbonates (Table S2), it is observed that the deposition of Ni results in significant reduction in surface area. Looking at the change of the pore volumes and peak pore sizes (Table S2) before and after Ni loading, it can be seen that MgCO_3 and NiO/MgCO_3 have similar total pore volume ($0.50 \text{ cm}^3/\text{g}$ and $0.46 \text{ cm}^3/\text{g}$ for MgCO_3 and Ni/MgCO_3 , respectively), while the pore size of MgCO_3 was approximately 3 times smaller than that of Ni/MgCO_3 (2.9 nm and 7.3 nm for MgCO_3 and Ni/MgCO_3 , respectively). Therefore, the loss in surface area upon NiO loading could be attributed to structural change and the loss of the small pores (e.g. due to sintering and pore blockage). [65] The morphology of the fresh and hydrogenated Ni/Ca, Ni/Ca1Mg1 and Ni/Mg are also examined by transition electron microscopy (TEM), as shown in Fig. 4. In all cases, Ni nanoparticles of similar size appear uniform dispersed on the carbonates before and after hydrogenation. During the reduction of Ni/Mg, apparent morphological changes are observed as the original cube-shaped of MgCO_3 particles (Fig. 4c) thermally decomposed to form irregular agglomerates of MgO , as shown in Fig. 4d. Nevertheless, the sizes of the Ni particles remain largely unchanged (around 10–20 nm) after hydrogenation, as listed in Table 1. No serious Ni sintering was observed (Fig. 4b, d and f). Looking at the EDS elemental maps of Ni, Ca and Mg elements of the Ni/Ca1Mg1 DFM (Fig. 4g, h and i), it is observed that the reduced Ni particles are well dispersed on both two types of carbonates without any specific preference.

The XRD patterns of the fresh and hydrogenated Ni/Ca and Ni/Mg

DFMs (i.e., NiO/CaCO_3 and NiO/MgCO_3 , respectively) are shown in Fig. 5a and b, which shows no obvious diffraction peak, suggesting the amorphous nature of the NiO-impregnated precursors. [66] After 2 h reduction in 10 vol% H_2 at 400°C (Fig. 5a), the amorphous CaCO_3 was transformed into the stable calcite phase, where the peaks at $2\theta = 23.1^\circ$, 29.4° , 36.0° , 39.5° , 43.3° , 47.5° , and 48.6° corresponds to the calcite (012), (104), (110), (113), (202), (018) and (116) reflections, respectively [ICSD-18166]. The minor diffraction peaks at $2\theta = 32.1^\circ$ and 53.8° , are indexed as the (111) and (220) reflections of CaO [ICSD-14922], respectively, suggesting that a small fraction of CaCO_3 was converted to CaO during reduction. At the same time, the diffraction peak at $2\theta = 44.8^\circ$ and 51.8° , i.e., Ni (111) and (200) [ICSD-52265], indicate the formation of Ni metal upon the reduction of the NiO precursor. In comparison, the hydrogenation of Ni/Mg DFM resulted in the complete transformation of MgCO_3 to MgO , which showed characteristic peaks at $2\theta = 37.2^\circ$, 42.8° , 62.0° [ICSD-9863], while NiO was transformed to metallic Ni. The observed trend in phase transformation agrees with the common understanding that MgCO_3 is thermodynamically unstable and decomposes at 400°C , while CaCO_3 remain relatively stable. [69,70] The surface compositions of the fresh and hydrogenated DFMs are examined by X-ray photoelectron spectroscopy (XPS), as shown in Fig. 5c and d. The Ni $2p_{3/2}$ spectra of the fresh and hydrogenated Ni/Ca DFM reflect the change in the chemical state of Ni, as shown in Fig. 5c. For fresh Ni/Ca DFM, the spectrum consists of a multiplet at 851.4 eV and 854.0 eV, both corresponding to NiO, and a satellite peak at 858.8 eV. For the hydrogenated Ni/CaCO₃, the Ni $2p_{3/2}$ binding energy changes to 854.2 eV with a satellite peak at 859.8 eV, which is attributed to the reduction of NiO and the formation of metallic Ni. [72, 73] Similarly, for Ni/MgCO₃, the reduction of NiO to metallic Ni is observed after the hydrogenation of the fresh Ni/Mg DFM, where a multiplet at 851.4 eV and 854.6 eV (corresponding to NiO) with its

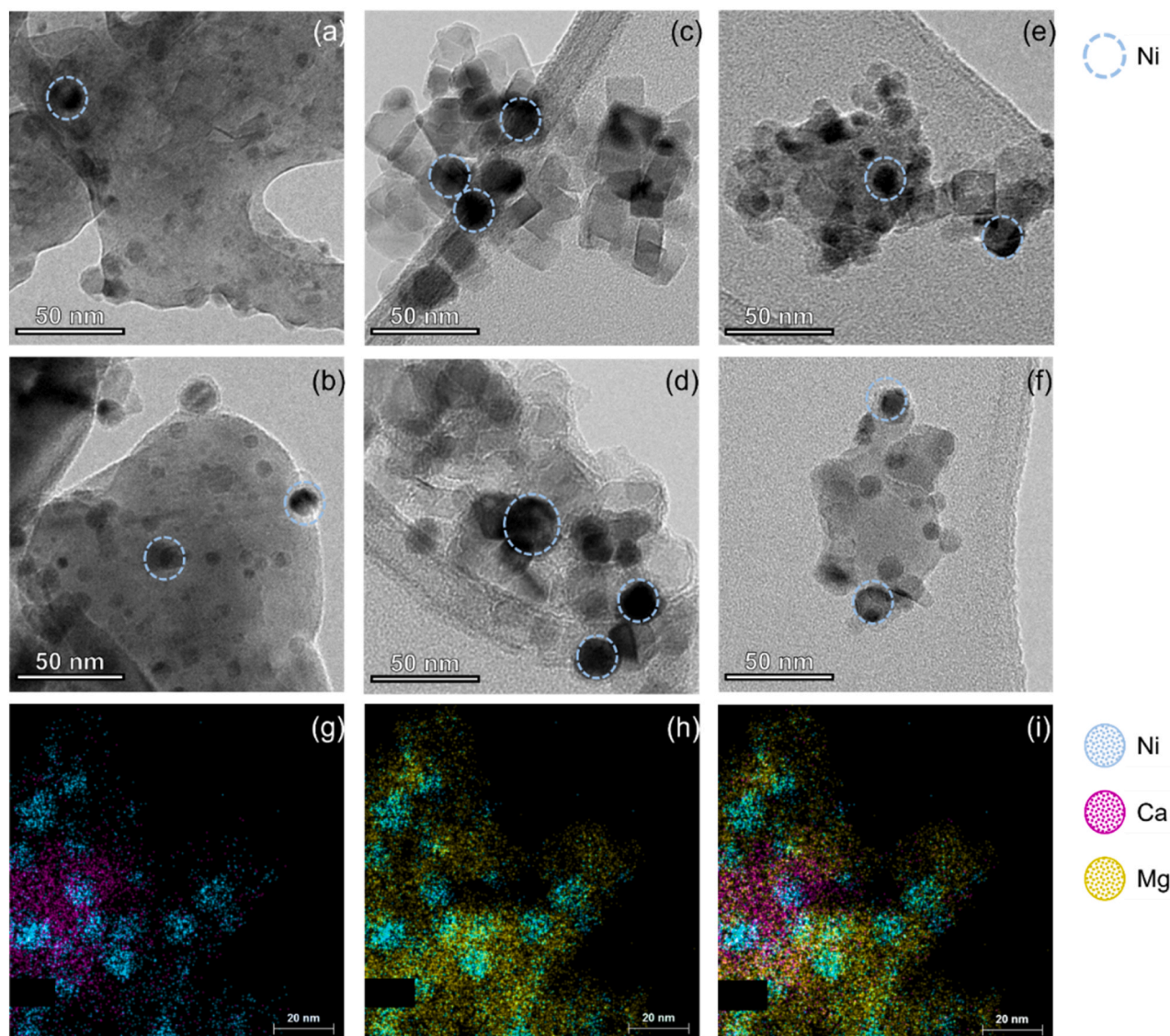


Fig. 4. TEM images of fresh and hydrogenated (a),(b) Ni/Ca; (c),(d) Ni/Mg; and (e),(f) Ni/Ca1Mg1; and EDS mapping images of (g) Ni-Ca, (h) Ni-Mg (i) Ni-Ca-Mg (i) hydrogenated Ni/Ca1Mg1.

satellite peak at 860.6 eV are presented. After the hydrogenation, the Ni $2p_{3/2}$ signal appears at 854.1 eV, suggesting the formation of metallic Ni on the surface of the hydrogenated Ni/MgCO₃ (Fig. 5d).

The extent of interaction between Ni and the carbonate or oxide supports are characterised by H₂-TPR of the fresh Ni/carbonate DFMs; the results are shown in Fig. 6a. Specifically, a TPR peak at higher temperatures suggests stronger metal-support interaction than a TPR peaks at a lower temperature. Accordingly, the TPR peaks can be categorised into 3 types according to the temperatures at which they occur: (i) 90–130 °C, which are assigned to the reduction of NiO not interacting with the support, e.g. bulk NiO, (ii) 150–200 °C, which are assigned to the reduction of NiO weakly interacting with the support, e.g. NiO at the NiO/carbonate interfaces, and (iii) > 800 °C, which are assigned to the reduction of NiO strongly interacting with the support, e.g. the formation of Ni-containing mixed oxide phases or solid solutions. For Ni/Mg, NiO strongly interacts with the support, exhibiting a large type (iii) TPR peak, with a small low-temperature peak corresponding to the formation of Ni metal, probably prior to the decomposition of MgCO₃. The strong interaction between NiO and MgO support could originate from the formation of a solid solution between the two halite-structured oxide phases (i.e. decomposed from MgCO₃), because the Ni²⁺ in a MgO-rich

solid solution is much more difficult to reduce than unsupported NiO. [74] With increasing CaCO₃ contents (i.e., Ni/Ca1Mg3 and Ni/Ca1Mg1), the type (ii) peak gradually intensifies, likely owing to the introduction of weak interaction between NiO and CaCO₃. When CaCO₃ contents become dominate (e.g., Ni/Ca3Mg1 and Ni/Ca), the type (iii) TPR peak almost vanishes; instead, type (i) and (ii) peaks become significant. For Ni/CaCO₃, the absence of any type (iii) peak further signify that the type (iii) interaction is exclusively associated with a Ni/MgO interface. [75] In conclusion, the metal-support interaction is strong across the Ni/MgO interface, but weak across the Ni/CaO or Ni/CaCO₃ interface. [76].

The surface Ni dispersion on the hydrogenated DFMs was quantitatively determined using the results of CO pulse chemisorption, as shown in Table 1. A stoichiometric factor of CO to Ni atom of 1:1 is assumed. From Table 1, it can be seen that hydrogenated Ni/CaCO₃ has a Ni dispersion of 3.9%, which increases to 5.9% upon the addition of Mg (i.e., Ni/Ca3Mg1). Subsequent increase in Mg content (i.e., Ni/Ca1Mg1, Ni/Ca1Mg3 and Ni/Mg) resulted in the progressive decrease in Ni dispersion. In the extreme scenario of Ni/Mg (i.e. Ni/MgO), the Ni dispersion is only 0.8%, which can be attributed to the formation of NiO-MgO solid solution, which suppress the formation of metallic Ni during

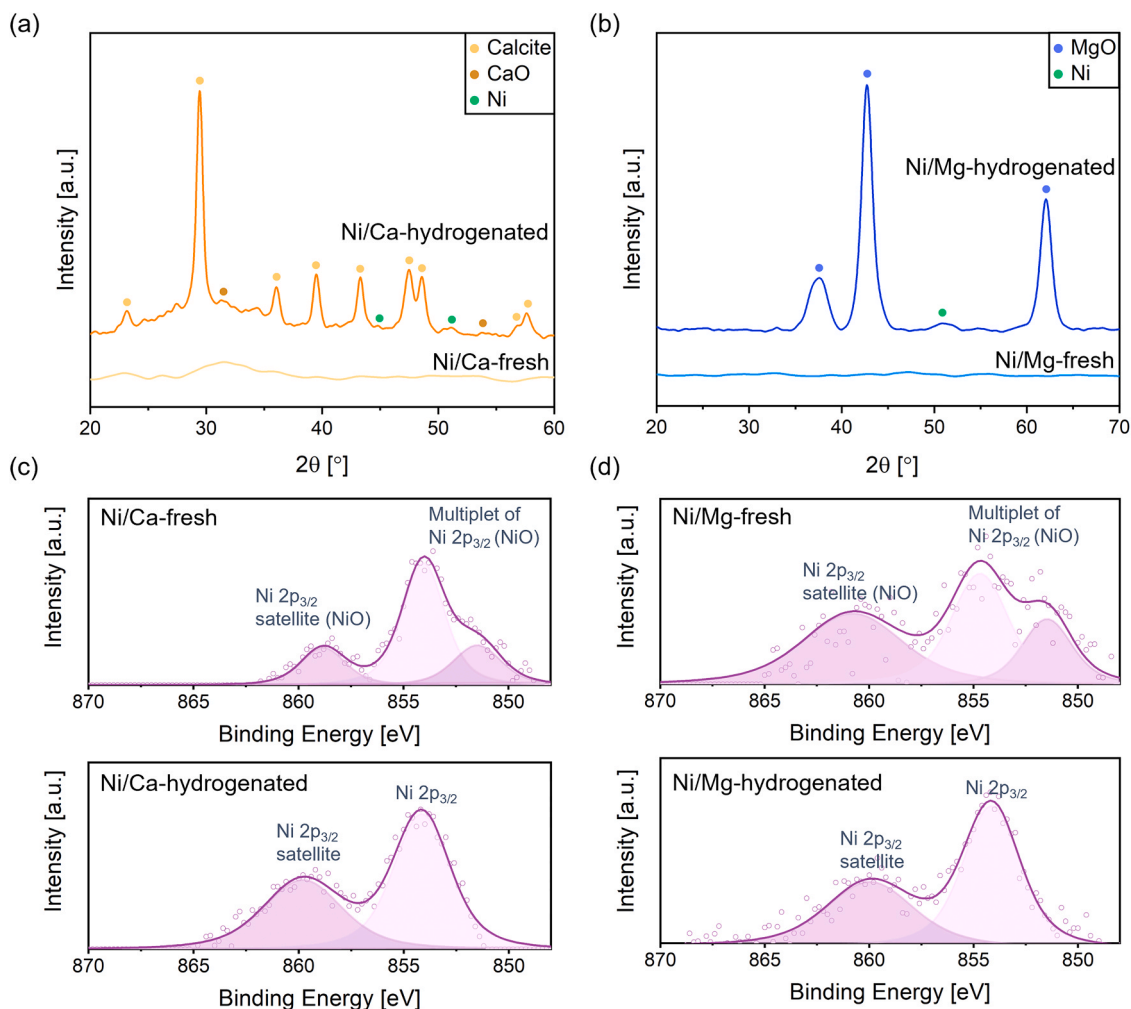


Fig. 5. XRD patterns of fresh and hydrogenated DFMs of Ni/Ca (a) and Ni/Mg (b); XPS Ni 2p_{3/2} spectra of over fresh and hydrogenated DFMs of Ni/Ca (c) and Ni/Mg (d).

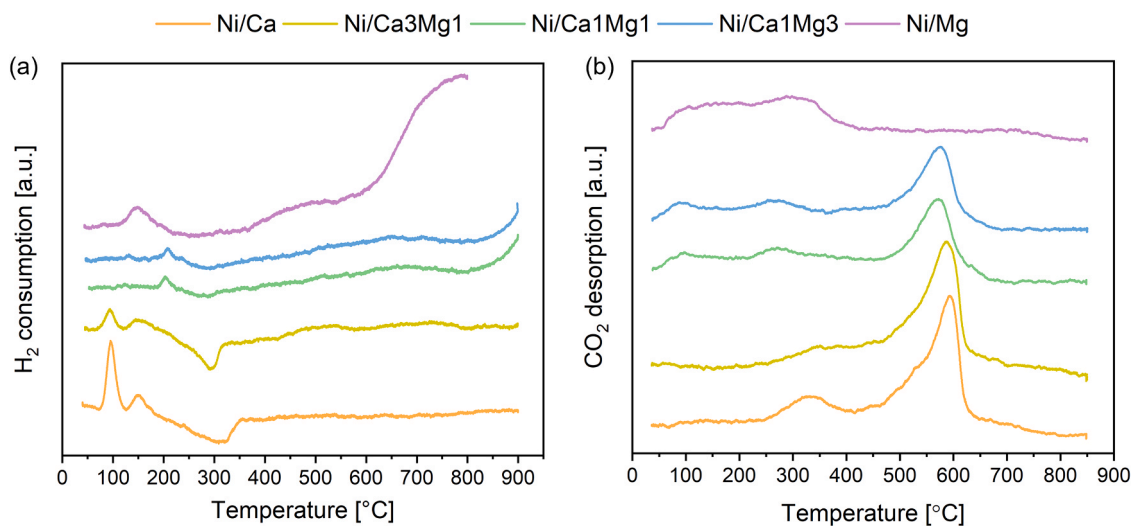


Fig. 6. (a) H₂-TPR and (b) CO₂-TPD results of the various Ni/carbonate DFMs.

reduction (i.e. during hydrogenation), [75] while the metallic Ni precipitated from the solid solution are expected to interact strongly with the MgO support.

Surface alkalinity and basicity is also an important property for both

CO₂ sorbents, CO₂ hydrogenation catalysts, [18] and DFMs. Here, CO₂-TPD is used to characterise the stability of the carbonates, which in turn reflects the surface basicity of the DFMs. In general, TPD peaks at higher temperatures correspond to high basicity and more stable

carbonates. As shown by the CO₂-TPD results in Fig. 6b, two broad peaks at ~100 °C and ~275 °C can be seen in the TPD profiles of the Mg-rich samples, signifying the weak basic sites of MgO. A sharp peak at ~570–590 °C was seen in all Ca-containing samples, representing the strong basic sites on CaO. Therefore, the surface basicity of these Ni/carbonate samples, as characterised by CO₂-TPD, reflects the alkalinities of the DFMs, i.e., Ca-rich DFMs has higher basicity than Mg-rich DFMs. According to the literature, moderate basicity, which corresponds to the TPD peaks at intermediate desorption temperatures would be ideal for catalytic CO₂ hydrogenation at moderate temperatures (~300–500 °C). [77] Tuning the surface basicity to suitable strength could promote interaction between the carbonates with the active metal sites, which enhances the CO₂ adsorption and hydrogenation to CH₄. [18,41,78] These moderate basic sites could be seen in the two Ca-rich samples (i.e., Ni/Ca and Ni/Ca3Mg1). During ICCU cycles, the surface basicity of the various DFMs could play important roles in determining the rate and selectivity of the hydrogenation of the captured CO₂. [79].

3.2. Direct hydrogenation of Ni/carbonates

Fig. 7a and b show the typical gas concentration profiles of CO, CH₄ and CO₂, when Ni/Ca1Mg3 and Ni/Ca, respectively, were heated up from room temperature to 400 °C in flowing hydrogen. Here, the temperature programmed hydrogenation (TPH) results of Ni/Ca1Mg3 and Ni/Ca are chosen as examples for discussing the typical product profiles observed during the experiments. The full set of TPH results of all the samples studied, viz. Ni/Mg, Ni/Ca1Mg3, Ni/Ca1Mg1, Ni/Ca3Mg1 and Ni/Ca are shown in the Supporting Information (Fig. S2). For Ni/Ca1Mg3 (Fig. 7a), as the sample was heated up in H₂, NiO is firstly reduced to metallic Ni below 200 °C to for the active sites for CO₂ and, or

carbonate hydrogenation. Then, a peak of CO₂ emerged, signifying carbonation decomposition, followed by a peak of CO and finally CH₄. The sequence at which the gaseous products appeared suggests that the corresponding reactions producing them might be mechanistically sequential, i.e., CO might be produced from the gaseous CO₂ product, while CH₄ might be produced from the CO intermediate. For Ni/Ca, however, very little CO₂ or CO gas was released. Instead, CH₄ was directly formed during the hydrogenation of Ni/Ca. Fig. 7c shows the total amount of 3 C-containing gases produced (i.e., CO, CH₄ and CO₂) during the temperature-programmed hydrogenation experiments. In general, the total amount of these 3 gases produced decreases with increasing Ca:Mg ratio. Ni/Mg produced the most C-containing gases, albeit primarily in the form of CO₂ (0.73 mmol) with trace amount of CO (0.02 mmol), whereas Ni/Ca produced the least amount, and mostly all in the form of CH₄ (0.12 mmol, while the amount of CO or CO₂ production was negligible). For Ni supported on mixtures of MgCO₃ and CaCO₃, the amount of each gas produced and the corresponding product selectivity are in between the extremes of Ni/Mg and Ni/Ca. The trend in the total amount of CO, CH₄ and CO₂ gases produced can be explained by the fact that MgCO₃ would fully decompose during the temperature programme, releasing gaseous CO₂. Ni/Mg produced little CO or CH₄ because little Ni sites were available from the incomplete reduction of the NiO-MgO solid solution. CO was only produced in samples containing MgCO₃, suggesting that the CO originated from the hydrogenation of gas phase CO₂, which re-adsorbed onto the catalyst sites and underwent RWGS. In contrast, the Ni/CaCO₃ interface yielded no gaseous CO₂, since CaCO₃ is largely stable at 400 °C. Nevertheless, a substantial amount of CH₄ (with nearly 100% selectivity) was produced from the hydrogenation of Ni/CaCO₃, suggesting that the CH₄ was produced via the direct hydrogenation of CaCO₃.

The temperatures at which the rate of production of the 3 gases reach

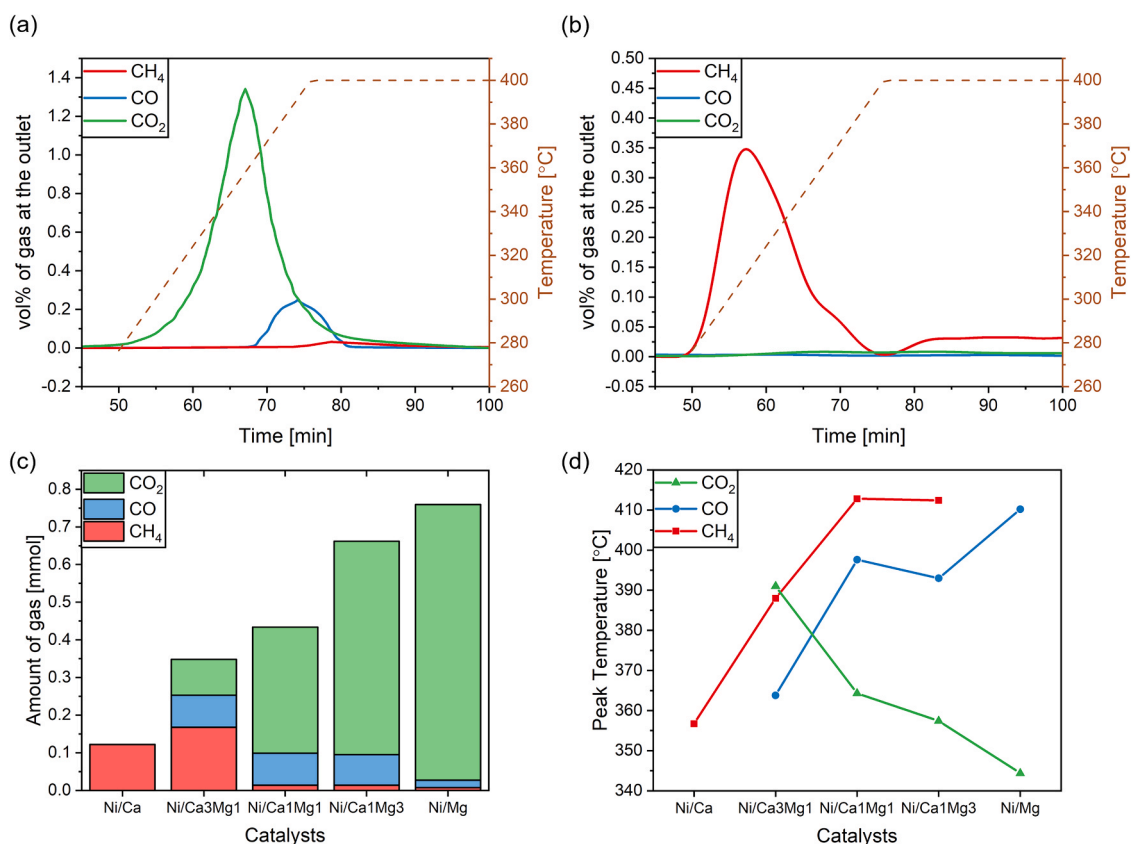


Fig. 7. Gas concentration profiles of CH₄, CO₂ and CO on Ni/Ca1Mg3 (a) and Ni/Ca (b) during direct hydrogenation from 50° to 400°C, following by isothermal hydrogenation at 400 °C, both in 10% H₂/N₂ at 1 atm; (c) amount of CH₄, CO and CO₂ formation during direct hydrogenation experiments; (d) peak temperatures of CH₄, CO and CO₂ formation during direct hydrogenation on Ni/carbonate DFMs.

maximum are deemed a characterisation of the reaction kinetics and plotted in Fig. 7d. As shown in Fig. 7d, as the Ca:Mg ratio increases, the temperature at which the rate of release of CO_2 maximises increases, because less and less MgCO_3 is available for thermal decomposition. For

example, the temperature at which the rate of release of CO_2 maximises was 344 °C for Ni/Mg sample, but when the Ca:Mg ratio was increased to 3:1, the corresponding peak temperature rose to 391 °C. Interestingly, the peak temperatures of both CO production and CH_4 production

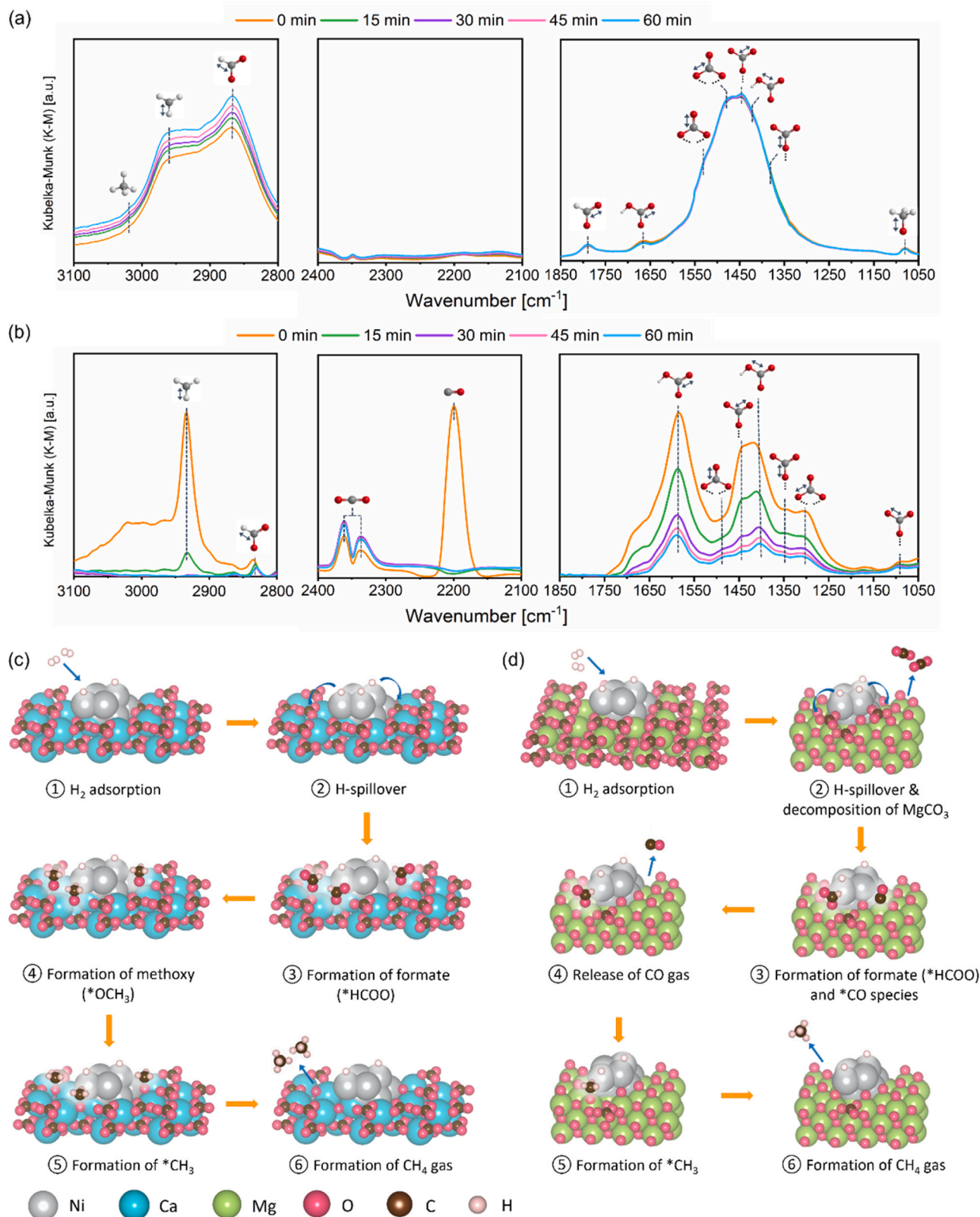


Fig. 8. Time-resolved in situ DRIFTS spectra of the direct hydrogenation of (a) Ni/Ca and (b) Ni/Mg in 25% H_2/Ar at 1 atm total pressure and 400 °C over 1 h. (c) and (d) schematically illustrate the proposed reaction mechanism of direct hydrogenation on Ni/Ca and Ni/Mg , respectively.

decrease with increasing Ca:Mg ratio, especially the peak temperature of CH_4 production greatly dropped from 412 °C for Ni/CaMg3 to 357 °C for Ni/Ca sample. This means high CaCO_3 content corresponds to enhanced rate of hydrogenation, suggesting that the presence of CaCO_3 kinetically favours the hydrogenation of carbonates or the surface-adsorbed CO_2 .

As discussed above and shown in Fig. 7, the temperature-programmed hydrogenation experiments suggest that the reaction pathways on Ni/MgCO₃ and Ni/CaCO₃ may be fundamentally different. The mechanistic origin of this difference is explored by in situ DRIFTS. Fig. 8a and b show the DRIFT spectra during the isothermal hydrogenation of Ni/CaCO₃ and Ni/MgCO₃ interfaces, respectively, at 400 °C. For Ni/CaCO₃ (Fig. 8a), IR signals corresponding to 3 different surface carbonate species can be seen: monodentate carbonates (1443 and 1385 cm^{-1}), bidentate carbonates (1539, 1497, 1298 and 1275 cm^{-1}), and bicarbonates (1660 and 1427 cm^{-1}). Upon hydrogenation, the intensities of these carbonate peaks were progressively weakened over time, indicating their consumption. Concomitantly, the peaks corresponding to formate species emerge at 2850, 1788 and 1462 cm^{-1} , implying the conversion of carbonates to surface formate groups by hydrogenation. [43,80–82] The gradual emergence of methoxy species ($^*\text{H}_3\text{CO}$) peaks at 1080 cm^{-1} as a possible product of formate hydrogenation, further suggests that the direct hydrogenation proceeds via the formate pathway on Ni/CaCO₃, with the hydrogenation of methoxy being one of the rate-determining steps. The proposed formate pathway is schematically depicted in Fig. 8c. Firstly, H_2 gas is dissociated on Ni sites to generate $^*\text{H}$ species, which spills over the interfacial CaCO_3 and reacts with the surface carbonates to form formate species. The formate species are successively hydrogenated by more $^*\text{H}$ from the neighbouring Ni sites, to generate $^*\text{H}_3\text{CO}$ and eventually $^*\text{CH}_3$, undergoing formate pathway for CO_2 methanation. Finally, upon hydrogenation of $^*\text{CH}_3$, CH_4 is produced and desorbed. The hydrogenation of CO_2 adsorbed species or surface carbonates over Ni sites upon the addition of H_2 , with formate species as key intermediates, was reported on a Ni- $\text{Na}_2\text{O}/\text{Al}_2\text{O}_3$ DFM for CO_2 capture and in situ methanation as well. [62].

Unlike Ni/CaCO₃, much weaker characteristic IR peaks of formate species are observed throughout the in situ DRIFTS experiment of Ni/MgCO₃, as shown in Fig. 8b. In addition to the gradual weakening of the

signals associated with surface carbonates and gaseous CO_2 due to MgCO_3 decomposition (2362 and 2337 cm^{-1}), a small formate peak, which also weakens over time, can be observed at 2832 cm^{-1} . At the same time, an intense peak corresponding to a surface-adsorbed CO species (2202 cm^{-1}) is also observed at $t = 0$ but quickly diminishes, [81] probably as a result of direct C=O cleavage of CO_2 or RWGS. [83, 84] Therefore, both the RWGS pathway and the formate pathway could be simultaneously present on Ni/MgCO₃. Given the weak formate peak relative to the intense CO peak, it is probably that RWGS dominates the reaction on the Ni/MgCO₃ sample, as schematically illustrated in Fig. 8d. For hydrogenation on Ni/MgCO₃ at 400 °C, firstly, MgCO_3 would decompose to MgO and then CO_2 gas is released. The released CO_2 would react with the $^*\text{H}$ species generated from H_2 dissociation on Ni sites to form either formate intermediate or get reduced to $^*\text{CO}$ species by RWGS pathway. The formed $^*\text{CO}$ species would be desorbed and produce CO gas, while the formate species are further hydrogenated to CH_4 gas by formate pathway.

The hydrogenation of Ni/Ca will directly transform CaCO_3 to CaO at a temperature where CaCO_3 is expected to be stable in conventional carbon capture cycles (e.g., 400 °C). To further investigate the hydrogenation behaviour and reaction model on Ni/CaCO₃, the hydrogenation duration of Ni/CaCO₃ was prolonged to 24 h. The rate of CH_4 formation and in situ DRIFTS during the 24 h hydrogenation experiment are shown in Fig. 9a and b, respectively. From Fig. 9a, there is an initial peak in the rate of CH_4 formation, which dropped to a steady value after 1 h. Correspondingly, the DRIFTS time series shows an initial quick drop of carbonate peak intensity in the first 0.5 h of the experiment, after which the intensities of the carbonate peaks stabilised. The evidence observed suggests the presence of two reaction phases: (i) a kinetically fast phase corresponding to the hydrogenation of CaCO_3 near the Ni/CaCO₃ interface and, or surface carbonates, followed by (ii) a slow phase corresponding to the hydrogenation of bulk CaCO_3 , as depicted Fig. 9d. The proposed two-phase reaction model is supported by experimental evidence previously reported in the literature. [19] An analysis of the TEM image of a Ni/CaCO₃ sample after 1 h of hydrogenation (Fig. 9c) further corroborate the reaction model. From Fig. 9c, it can be seen that, after 1 h of hydrogenation, a Ni particle is surrounded by CaO (with lattice fringes of 0.267 nm, assigned to CaO (111) plane) as a result of the direct hydrogenation of CaCO_3 during the fast stage. At > 5 nm away

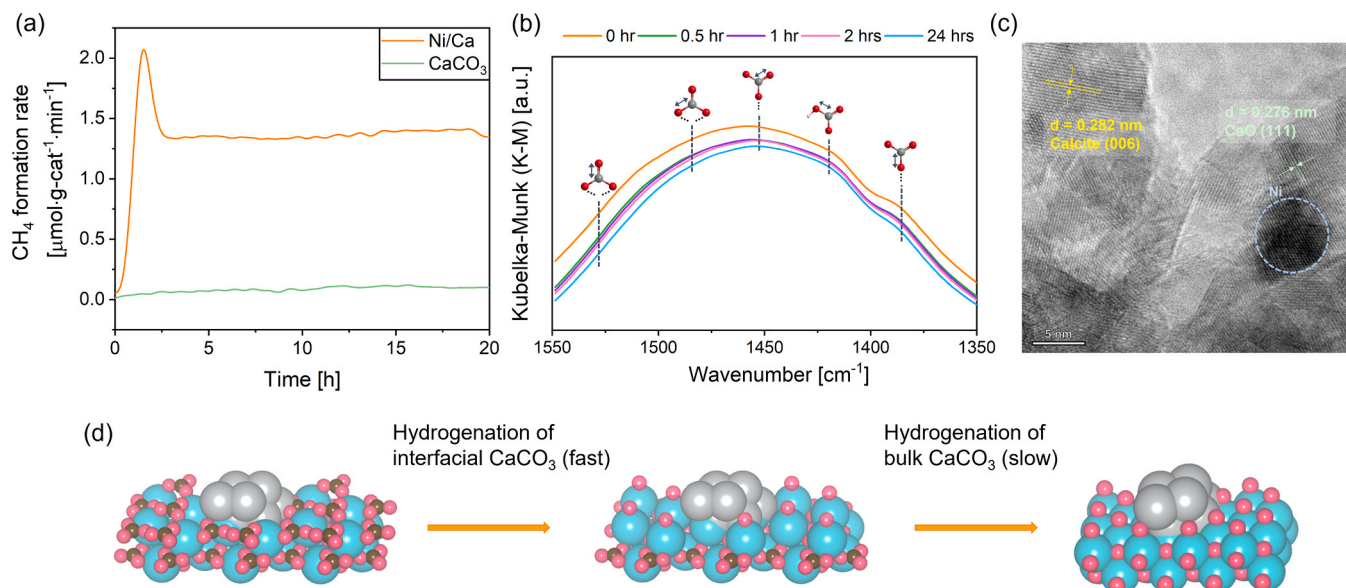


Fig. 9. (a) Gas profile of rate of CH_4 formation during the hydrogenation (in 10% H_2/N_2 at 1 atm total pressure) of Ni/Ca and unloaded CaCO_3 at 400 °C over 20 h. (b) in situ DRIFTS spectra showing the evolution of surface carbonate species during the hydrogenation of Ni/Ca (in 10% H_2/N_2 at 1 atm total pressure) at 400 °C over 24 h. (c) TEM image of a hydrogenated Ni/CaCO₃ sample; the blue circle indicates a Ni particle. (d) Schematic illustration of the progressive hydrogenation of Ni/CaCO₃ over time.

from the Ni particle, CaCO_3 (with lattice fringes of 0.282 nm, corresponding to calcite (006) plane) remains present and yet to be hydrogenated by the slow stage. However, the exact nature of the reaction front and the associated mass transfer scheme for this slow phase, be it (i) hydrogen spill over, (ii) diffusion of carbonate species, (iii) transfer hydrogenation via the diffusion of hydrogenated intermediates or (iv) a combination of all of the above, is not clear and merits further investigation in future studies.

3.3. Integrated CO_2 capture and utilisation cycles

The evolution of the Ni/carbonate interfaces is investigated by subjecting the samples to 15 cycles of CO_2 capture and hydrogenation, as shown in Fig. 10. Fig. 10a shows the gas concentration profiles of CO , CH_4 and CO_2 at the reactor outlet during the first, second, third, 13th, 14th and 15th ICCU cycles, when Ni/Ca was used as the DFM. In each cycle, CH_4 is the dominating product during the hydrogenation stage, while trace amount of CO was generated during the CO_2 capture stage. The latter can be possibly explained by (1) the oxidation of surface Ni atoms by CO_2 , [17] or (2) the RWGS reaction between the incoming CO_2 gas and chemisorbed H_2 on the Ni surface, formed during the previous hydrogenation step. [60] The total amount of gaseous product formed in each cycle, over 15 ICCU cycles is shown in Fig. 10b. In general, more CH_4 is formed on samples that are richer in CaCO_3 , in line with the trend shown in Fig. 6. In the 15th cycle, the amount of CH_4 formed on Ni/Ca (1.28 mmol/g) is 23.5 times of that on Ni/Mg (0.054 mmol/g), showing a significant disparity in their methanation activity. Moreover, Ni/Ca sample could produce a relatively consistent amount of CH_4 per cycle, from the 3rd cycle onwards, whereas the other DFMs show significant decay in their ability to produce CH_4 . In addition to sintering, which would result in the reduction in surface area available for CO_2 conversion and destruction of pore structure that are essential to efficient mass transfer, the rapid deterioration of the Mg-containing DFMs may also be attributed to the gradual and irreversible consumption of carbonates (both MgCO_3 and CaCO_3) over consecutive cycles without effective

regeneration. In contrast, the cyclic CO yield is consistent throughout the 15 cycles, regardless of the composition of the DFMs.

As shown in Fig. 9, both surface and bulk CaCO_3 can be hydrogenated to produce CH_4 . To examine whether all the CH_4 produced by Ni/Ca is a result of hydrogenation of regenerable carbonates (instead of a cumulative and irreversible consumption of pre-formed CaCO_3 in the sample), we repeated the ICCU cycling experiment using a pre-calcined Ni/Ca (i.e. Ni/CaO) as the starting material. The pre-calcination was done by subjecting Ni/ CaCO_3 in 100 mL/min N_2 at 850 °C for 1 h to fully decompose the CaCO_3 support to CaO. The corresponding results, as shown in Fig. 10c, indicate that the pre-calcined Ni/Ca (i.e., Ni/CaO) shows a similar cyclic performance of CH_4 production over 15 ICCU cycles, with the exception of the first cycle, in which no carbonate was available in Ni/CaO to hydrogenation. Similar amount of CH_4 was produced by Ni/CaO in each cycle (e.g., ~1.26 mmol/g at the 7th cycle, as shown in Fig. 10c) as the experiment starting with Ni/ CaCO_3 . In addition, as shown in Fig. S3, the profiles of rate of production of CH_4 by the hydrogenation of a Ni/CaO DFM are similar to those of a Ni/ CaCO_3 DFM (Fig. 10a), depicting the both fast hydrogenation of the surface carbonate and the slow hydrogenation of the bulk carbonate. Therefore, the results of this control experiment confirm that both the surface and the bulk CaCO_3 that is consumed (hydrogenated) from Ni/Ca in each ICCU cycle can be regenerated in the subsequent cycle. Furthermore, by comparing the total amount of CH_4 formation during the hydrogenation step with the amount of CO_2 available in the surface monolayer of Ni/ CaCO_3 (Table S3) it is clear that both CO_2 capture and carbonate hydrogenation of Ni/ CaCO_3 involves reactions beyond the surface monolayer. Accordingly, approximately 10.5% of all the carbonate available in Ni/ CaCO_3 participates in the ICCU cycles, under the given operating conditions.

Fig. 11a and b show the diffraction patterns of the Ni/Ca and Ni/Mg samples after 15 ICCU cycles. Similar to the hydrogenated samples shown in Fig. 9c, which represent hydrogenated DFMs experiencing the first cycle, metallic Ni, calcite and CaO are both present in the cycled Ni/Ca in its hydrogenated state. For Ni/MgO, only MgO can be observed. No

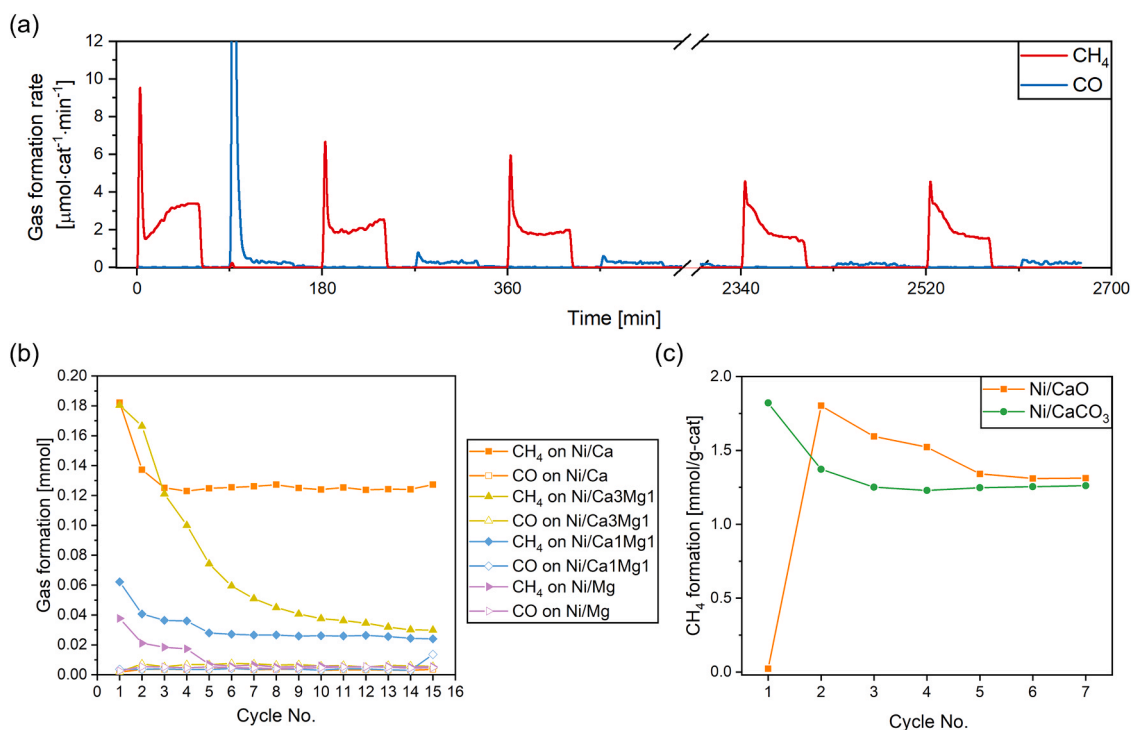


Fig. 10. (a) CH_4 and CO profiles during two-step CO_2 capture and hydrogenation on Ni/Ca over 15-cycles at 400 °C; (b) Results of two-step CO_2 capture and hydrogenation over 15-cycles at 400 °C: amount of CH_4 and CO formed during the hydrogenation and capture stages, respectively, in each cycle; (c) Amount of CH_4 formation on Ni/Ca starting from Ni/CaO and Ni/ CaCO_3 over 7 ICCU cycles.

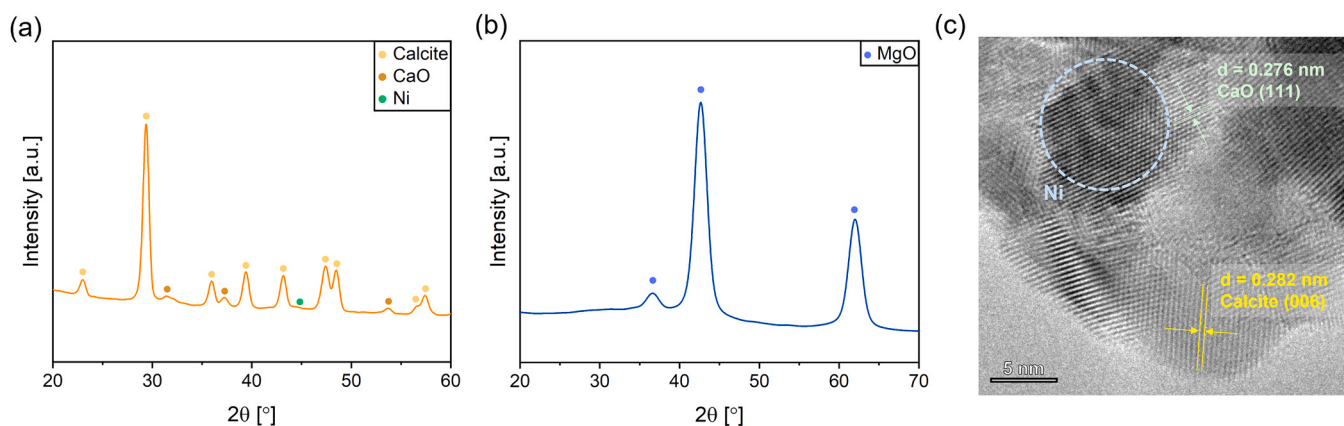


Fig. 11. XRD patterns of cycled catalysts of Ni/Ca (a) and Ni/Mg (b) after 15 ICCU cycles; (c) TEM image with lattice fringes of cycled Ni/Ca catalysts after 15 cycles of CO_2 capture-hydrogenation.

diffraction peak of Ni could be observed in the XRD of the cycled samples, probably because of the small sizes of Ni particles, as well as the formation of NiO-MgO solid solution mitigating the formation of Ni particles. The TEM image of cycled Ni/Ca, as shown Fig. 11c, reveals a structure that is highly similar to a freshly hydrogenated Ni/Ca (Fig. 9c), i.e., a nickel nanoparticle is surrounded by CaO, while CaCO_3 can be observed further away. In conclusion, in the case of Ni/Ca DFM, the reaction pathway, catalytic mechanism, catalyst structure and reaction model remain largely unchanged over ICCU cycles. Therefore, the findings in the present study should be relevant to understanding the

behaviour of DFMs over long term ICCU operations.

4. Discussion

The hydrogenation of a carbonated catalyst surface is often used to examining the catalytic mechanism of conventional CO_2 hydrogenation reactions. Here, we examine the analogy between the performance of DFMs over ICCU cycles and that during conventional CO_2 hydrogenation. Fig. 12a and b show the CO_2 conversion and CH_4 selectivity when the five Ni/carbonate DFMs are used as conventional CO_2

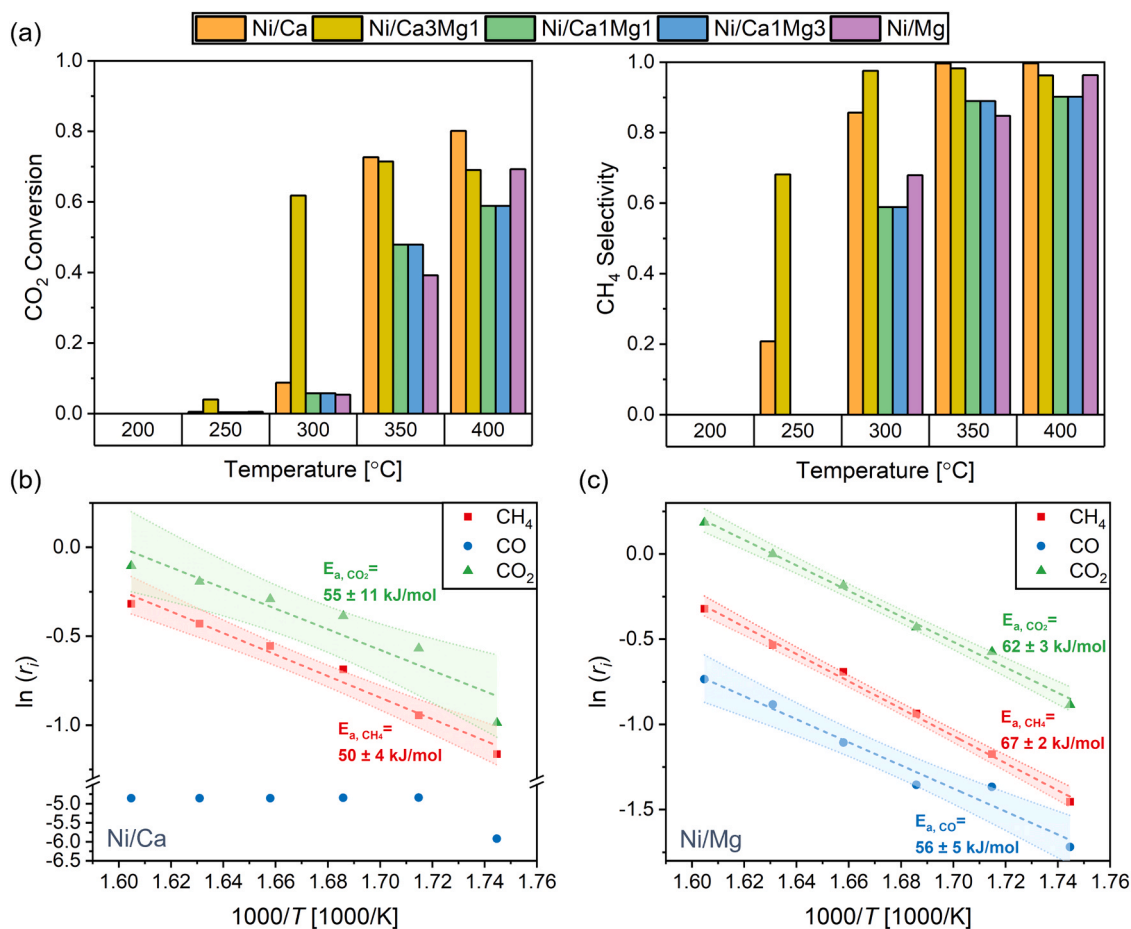


Fig. 12. (a) Conventional one-step CO_2 methanation performance test results on 8 wt% Ni loading samples ($\text{H}_2:\text{CO}_2 = 4:1$); Arrhenius plots of CH_4 formation, CO formation and CO_2 consumption during catalytic CO_2 hydrogenation on (b) Ni/Ca and (c) Ni/Mg.

hydrogenation catalysts over the temperature range of 200–400 °C. For all 5 samples, the CO₂ conversion and CH₄ selectivity increased with increasing temperatures. Fig. 12a shows that, among all samples, Ni/Ca achieved the highest CH₄ yield of 80.0% with a CH₄ selectivity of near unity (>99%), corresponding to a specific CH₄ formation rate of 105.6 $\mu\text{mol}\cdot\text{s}^{-1}\cdot\text{g}^{-1}$ at 400 °C. The two Ca-rich supports, Ni/Ca and Ni/Ca₃Mg₁, exhibited higher CO₂ conversion and higher CH₄ selectivity at moderate temperatures from 300° to 350°C than the other 3 Mg-rich samples. In fact, at any given temperature, samples richer in Ca tend to show higher CO₂ conversion and higher CH₄ selectivity. However, the difference in CO₂ conversion and CH₄ selectivity between different samples are far less profound during conventional CO₂ hydrogenation than during ICCU cycles, in which Ni/Mg shows significantly low CH₄ yield and CH₄ selectivity (96% CH₄ selectivity during conventional CO₂ hydrogenation, while 53% CH₄ selectivity on 15th ICCU cycle at 400 °C). Such disparity suggests that the sources of CO₂ may be fundamentally different during conventional CO₂ hydrogenation and ICCU cycles. For conventional hydrogenation, all CO₂ comes from the gas feed. During ICCU, the reaction on Ni/MgCO₃ relies on a continuous supply of CO₂ in the gas phase, whilst the reaction on Ni/CaCO₃ would proceed via the direct hydrogenation of readily available carbonates, both at the surface and in the bulk.

The differences in the catalytic performance of Ni/Ca and Ni/Mg during conventional CO₂ hydrogenation and ICCU suggests that the different metal-support interfaces (Ni/CaCO₃ vs Ni/MgCO₃) and their subsequent interactions could lead to different CO₂ hydrogenation reaction pathways. In conventional CO₂ hydrogenation, 3 reaction pathways have been proposed: (1) direct C=O bond cleavage followed by possible CO hydrogenation, (2) RWGS followed by CO hydrogenation, and (3) the hydrogenation of formate (i.e., the formate pathway). [83, 85,86] The first two pathways involve the formation of *CO as a key intermediate, while the last involves the hydrogenation of CO₂ or carbonate to formate, which is further hydrogenated.

To probe the relationship between CO formation, CH₄ formation and CO₂ activation, the activation energies of CO formation ($E_{a,\text{CO}}$), CH₄ formation (E_{a,CH_4}) and CO₂ consumption (E_{a,CO_2}) during conventional CO₂ hydrogenation on Ni/Ca and Ni/Mg were determined based on the specific rates measured at low CO₂ conversions (<20%). [87] The results are shown in Fig. 12b and c. For Ni/Mg, $E_{a,\text{CO}}$ (56 ± 5 kJ/mol) < E_{a,CH_4} (67 ± 2 kJ/mol), meaning that the formation of CO is energetically favoured over the formation of CH₄. At the same time, $E_{a,\text{CO}}$ (56 ± 5 kJ/mol) < E_{a,CO_2} (62 ± 3 kJ/mol), suggesting that CO formation is possibly a prerequisite to CH₄ formation. For Ni/Ca, the amount of CO formation is too little to accurately estimate $E_{a,\text{CO}}$, while the activation energy of CH₄ is 50 ± 4 kJ/mol, similar to the activation energy of CO₂ of 55 ± 11 kJ/mol, suggesting that CO* is an unlikely intermediate for CO₂ methanation. Therefore, CO₂ hydrogenation on Ni/Ca is most likely to proceed via the formate pathway. [83,84].

To complement the analysis of apparent activation energies. The difference in reaction pathways on Ni/MgCO₃ and Ni/CaCO₃ are also examined by measuring the surface significant species during conventional CO₂ hydrogenation using in situ DRIFTS. On Ni/CaCO₃, both formate and methoxy species are observed, together with peaks corresponding to gaseous CH₄ at 3015 cm⁻¹, as shown in Fig. 13a. The observed peak can be explained by the formate pathway, in which the carbonate species is firstly hydrogenated to formate (*HCOO), which is successively hydrogenated to form methoxy (*H₃CO), methyl *CH₃ (showing a peak in 2966 cm⁻¹) and eventually gaseous CH₄. [83,84] The reaction pathway is schematically illustrated in Fig. 13c, which is similar to the formate pathway for proposed for Ni/CaCO₃ during ICCU cycles. On Ni/MgCO₃, the same surface species could be observed, albeit with much lower intensities of formate species, indicating that the formate pathway is insignificant on Ni/MgCO₃ (Fig. 13b). Furthermore, the peaks corresponding to CO gas (2294 and 2143 cm⁻¹) are observed, [83, 84] that direct CO₂ dissociation and/or RWGS pathway is prevailing on

Ni/MgCO₃, as schematically depicted in Fig. 13d. [88].

The experimental results have provided conclusive evidence showing that CO₂ hydrogenation on Ni/CaCO₃ and Ni/MgCO₃ are likely to proceed via formate and CO intermediates, respectively. Specifically, the CO (RWGS) pathway is responsible for the high CO yield and the low CH₄ selectivity on Ni/MgCO₃ (53% CH₄ selectivity on 15th ICCU cycle at 400 °C), in agreement with the experimental observations during both conventional CO₂ hydrogenation and ICCU cycles. In contrast, the Ni/CaCO₃ interface facilitates the efficient hydrogenation of carbonate to formate, which could be further hydrogenated at the metal/carbonate interface, facilitated by hydrogen spill over. This enhanced formate pathway is likely to arise from the interactions between Ni and CaCO₃, the moderate stability of CaCO₃, as well as the moderately alkalinity of Ni/CaO.

Based on the discussion so far, it is conducive that an efficient formate pathway may be the key for achieving high CH₄ yield and high CH₄ selectivity during both ICCU and conventional CO₂ hydrogenation. In the present study, experimental investigations under both ICCU and conventional CO₂ hydrogenation conditions suggest that the reaction pathway and catalytic mechanism under the two operating regimes may be related: formate pathway is dominating during both the hydrogenation of a Ni/CaCO₃ interface during ICCU and the hydrogenation of adsorbed CO₂ during conventional catalytic CO₂ methanation on Ni/CaCO₃. In comparison, Ni/MgCO₃ exhibits high selectivity towards the production of CO via the RWGS pathway, while methanation reaction via the formate pathway may also be feasible in the presence of a substantial CO₂ pressure (e.g. in the case of co-feeding gaseous CO₂ and H₂). Admittedly, the surface coverage of CO₂ on the DFMs under the two operating regimes may be rather different, i.e., the DFM would have a lower CO₂ coverage during direct hydrogenation than during conventional CO₂ hydrogenation. However, the structure and chemical nature of the bifunctional metal/carbonate interface, may play a more dominant role in determining the reaction mechanism during CO₂ transformation than the partial pressure of CO₂ and surface coverage within the operating regime of interest. This means that the hydrogenation of CO₂ may proceed via similar reaction pathways with similar rate-determining steps (e.g., the hydrogenation of formate, etc) for the two reaction regimes. Indeed, it is experimentally observed that the apparent CH₄ product yield and selectivity measured under both ICCU cycles and conventional CO₂ hydrogenation conditions share a similar trend, i.e. higher CaCO₃ content corresponds to higher CH₄ selectivity, as illustrated by a correlation plot shown in Fig. 14. In other words, the two-step carbonation-hydrogenation cycles (ICCU cycles) could be employed as an insightful approach to study the catalytic conversion of CO₂ on DFMs as well as other hydrogenation catalysts. Lastly, it should be noted that, in foreseeable commercial applications, there may be an even greater disparity between the operating conditions of ICCU and those of conventional hydrogenation, e.g., the DFM would be exposed to considerable partial pressures of oxygen, moisture and other impurities during ICCU [16,42]. Therefore, whether the observed correlation in reaction pathway and catalytic mechanism between the two regimes still hold should be experimentally verified in future studies.

5. Conclusion

The two-step CO₂ capture-hydrogenation process, using Ni-based DFMs, is studied on a model Ni/carbonate structures over moderate temperature ranges of 300–400 °C. The hydrogenation behaviour of Ni/CaCO₃ and Ni/MgCO₃ interfaces are found to be drastically different. Based on the in situ DRIFTS results, on Ni/CaCO₃, the hydrogenation reaction proceeds via the direct hydrogenation to carbonate, via formate, methoxy and methyl intermediates, eventually forming CH₄. On Ni/MgCO₃, the reaction proceeds following the thermal decomposition of MgCO₃ to produce gaseous CO₂, which subsequently adsorbs at the Ni/MgO interface to produce CO, which can be further hydrogenated to CH₄ with low CH₄ selectivity. Over 15 ICCU cycles at 400 °C, the

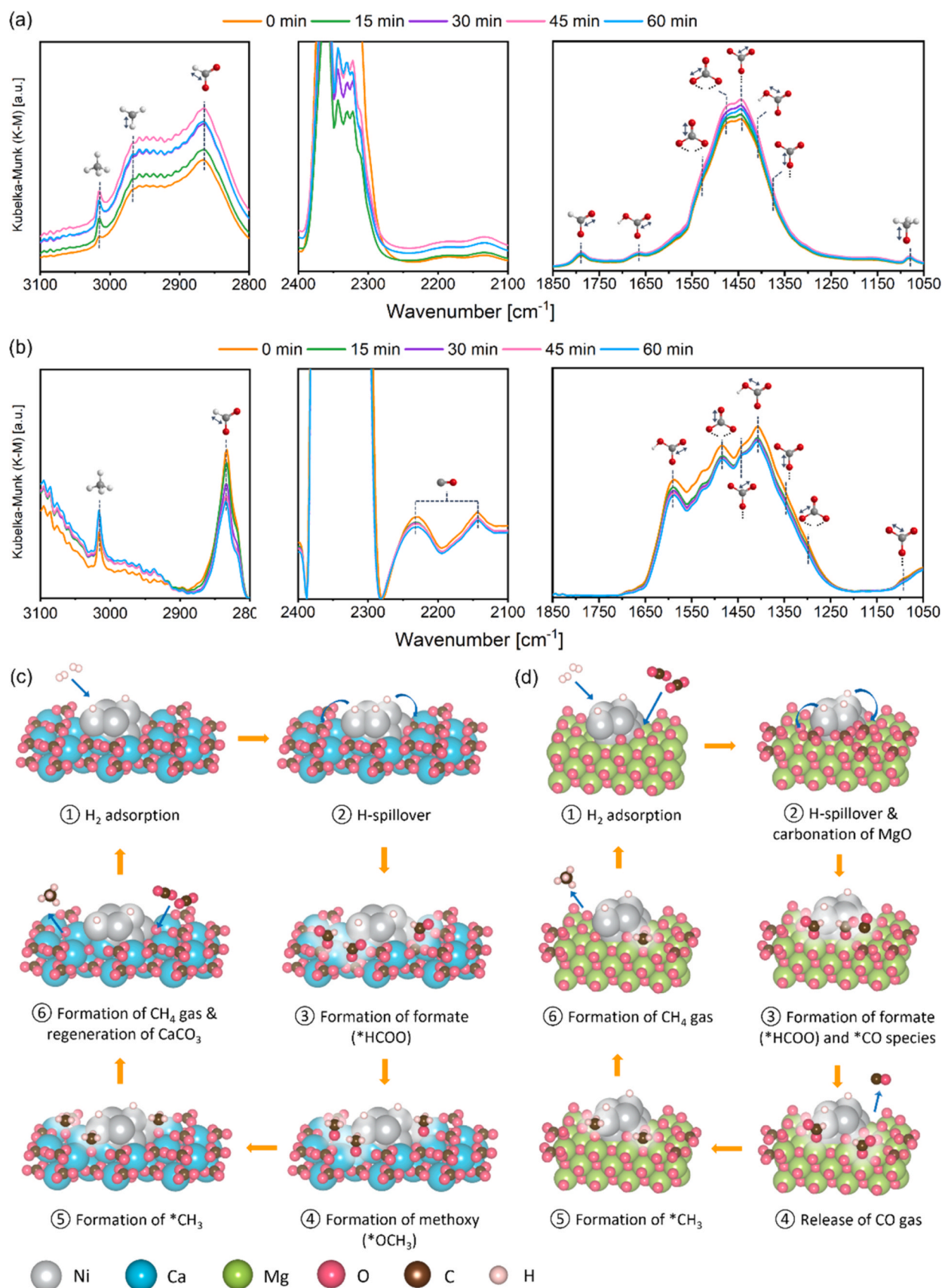


Fig. 13. in situ DRIFTS measurements on Ni/Ca (a) and Ni/Mg (b) at 400 °C under conventional CO_2 hydrogenation conditions in 40 mL gas mixture of $\text{CO}_2/\text{H}_2/\text{Ar} = 5/20/15$ (i.e., co-feed CO_2 and H_2); (b) proposed reaction mechanism of conventional CO_2 hydrogenation on (c) Ni/Ca and (d) Ni/Mg catalysts.

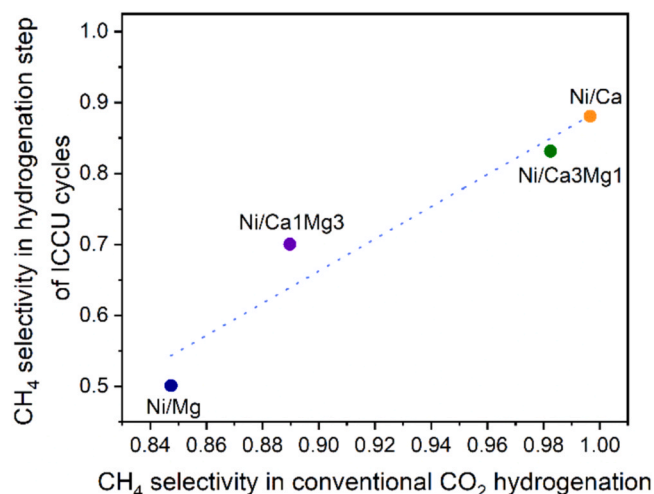


Fig. 14. Correlation between CH_4 selectivity between the direct hydrogenation step during ICCU cycles (10 vol% H_2/N_2 , 400 °C) and conventional CO_2 hydrogenation with co-feed of CO_2 and H_2 ($\text{H}_2/\text{CO}_2=4/1$, 350 °C) for the various DFM formulations.

structure, CO_2 capture performance and catalytic performance of Ni/Ca remains stable, affording a cyclic CH_4 yield of approximately 1.25 mmol/g with a CH_4 selectivity of near-unity, while both surface carbonate and bulk carbonate participate in the reaction, with the former proceeds at notably faster rates. The superior performance of Ni/Ca DFM could be attributed to it having sufficient moderate and strong basic sites (as characterised by CO_2 -TPD), as well as the unique metal-support interaction across the Ni/ CaCO_3 interface (as characterised by H_2 -TPR) that favours the hydrogenation of carbonates via the formate pathway.

Lastly, we report a strong correlation between the reaction mechanism and product selectivity of the ICCU cycles and those of conventional CO_2 hydrogenation; this correlation could be exploited for elucidating catalytic mechanisms for the hydrogenation of immobilised CO_2 or carbonate.

CRediT authorship contribution statement

Xianyue Wu: Formal analysis, Investigation, Visualization, Writing – original draft. **Ribooga Chang:** Formal analysis, Investigation. **Mingwu Tan:** Investigation. **Longgang Tao,** Investigation. **Qianwenhao Fan:** Investigation. **Xiaochun Hu:** Investigation. **Hui Ling Tan:** Investigation. **Michelle Åhlén:** Investigation. **Ocean Cheung:** Conceptualization, Writing – review & editing, Supervision. **Wen Liu:** Conceptualization, Writing – review & editing, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

Data will be made available on request.

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Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.apcatb.2023.123053.

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